Final Report to AOARD in 2005

Title of Research Project: *Self Assembled Nano-Photonic Devices Derived from Marine DNA for Opto-Electronic Applications*

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Summary

Research 1 Optical and photochromic properties of spiropyran-intercalated DNA-surfactant complex films for optical switching

Optical and photochromic properties of spiropyran-intercalated DNA-surfactant complex films were studied to aim at optical switching. They strongly depended on the type of spiropyran as well as the type of surfactant. Spiropyrans containing the oxazine ring and intercalated into DNA showed a very rapid photochromic response. It is also shown that photochromic response times became much faster by increasing the intensity of the excitation light.

Research 2 Optically-controlled photonic switches based on spiropyran-doped DNA-lipid complex films

Optical switching properties based on the photochromism of spiropyran-doped DNA-lipid complex films have been studied. On-off switching of the incident light under the alternate excitation of UV- and visible light showed strong dependence of the intensity of the excitation light. We have obtained the switching times of around 200-300ms, but much faster response could be expected since the proportional tendency has not been saturated yet.

Research 3 Structure-property relations of intercalated and chelated DNA-lipid complexes

Various DNA-cationic lipid complexes and their bulk films were

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14. ABSTRACT
Optical and photochromic properties of spiropyran-intercalated DNA-surfactant complex films were studied for optical switching. The switching speed was observed as 200-300 ms. They depended on the type of spiropyran as well as the type of surfactant. Spiropyrans containing the oxazine ring and intercalated into DNA showed a very rapid photochromic response. It also showed that photochromic response times became much faster when intensity of the excitation light increased. Various DNA-cationic lipid complexes and their bulk films were also prepared and their physical properties were measured.

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prepared and their physical properties were measured. Consequently, it was found that physical properties were greatly dependent on each lipids. The DNA-lipid complexes film formed by C-12 lipid of single-chain trimethylammonium type showed the largest value on mechanical strength. Water absorption behaviors of the films were also dependent on kinds of lipids. It was found that fluorescence quantum yields of cyanine dye-intercalated DNA-lipid films decreased nonlinearly with increasing relative humidity, while the fluorescence quantum yields were high compared with that of PMMA in whole range of relative humidity. Orientation of DNA molecules under magnetic field was carried out in order to enhance dye orientation within intercalated DNA molecules.

Research 4 Fabrication of intercalated DNA-lipid complexes to fibers and films

Developments of novel optical fibers derived from Marine DNA were carried out by a melt-spinning method in order to study optical characteristics of DNA fibers which were greatly improved by intercalating organic dyes into base pair layers of DNA molecules. Results indicated that the DNA-CTMA optical fiber was very much promising for light amplification.

Research 1 Optical and photochromic properties of spiropyran-intercalated DNA-surfactant complex films For optical switching

1. ABSTRACT

Optical and photochromic properties of spiropyran-intercalated DNA-surfactant complex films were studied to aim at rapid optical switching. They strongly depended on the type of spiropyran as well as the type of surfactants. Spiropyrans containing the oxazine ring which were intercalated into DNA showed a very rapid photochromic response. It was also shown that photochromic response times became much faster by increasing the intensity of the excitation light.

1. INTRODUCTION

Recent research results on DNA-surfactant complexes have shown various attractive features by the intercalation of some organic dyes into DNA films. We have already reported[1-□] basic optical characteristics, such as refractive indices, absorbance and fluorescence intensity, and photochromic properties, of spiropyran-intercalated DNA-cetyltrimethilammonium (CTMA) complex films, which were derived from marine biopolymers, DNA. Although DNA-surfactant (lipid) complexes showed promising potentials for optical functional devices such as switching or signal processing devices, their response speeds were relatively slow[4] to apply them to practical systems. Molecular-chemical bond state of DNA and surfactant in DNA-surfactant complexes depends on the kind of surfactant, and consequently optical or photochemical features of DNA-surfactant complexes will differ from each other according to the surfactant. This may also affect the response speed, and there maybe an possibility to improve the response speed much faster.

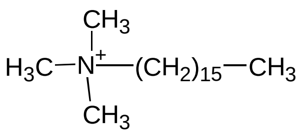
In this report, we report optical and photochromic properties of DNA-surfactant complex films intercalated by several different types of spiropyran compounds. In addition, we also report the effect of different kinds of surfactant on the photochromic properties. It was found that the absorption and fluorescence spectral intensity and photochromic reaction of those films strongly depended on the type of spiropyran. Also we found that the structural difference of the intercalated spiropyran caused the difference in the photochromic response time. The group of spiropyrans which include naphthalene and oxazine ring showed faster photochromic effect. Moreover, it was found that the selection of the surfactant strongly influenced the optical and photochromic properties of DNA-surfactant films. Increased fluorescence intensity was observed for DNA-surfactant films with double-chain dimethylammonium, compared with single-chain trimethylammonium type surfactants. These results suggest that the difference in the structure of the surfactant leads to the difference in the molecular-chemical bond state, and thus influenced the structural change of the spiropyran for the photochromic reaction.

2. Effect of Lipids on Optical Properties of Three Kinds of DNA-Lipid Complexes Doped by Spiropyran

Recently, DNA-lipid complexes have attracted much attention due to their functionality produced by doping of various organic dyes. Especially, the photochromic effect of DNA-lipid complexes have been expected to add a new functionality, such as ultra-fast optical switching, logical circuits, memory, etc., for next generation optical systems.

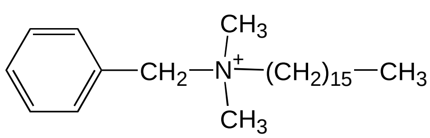
We have reported that DNA-lipid complexes preserved high-transparency for visible light and thermal stability, with nano-size free volume between base-pairs. Also the reports have revealed increased lasing and nonlinear properties by doping organic dyes into DNA. In addition to these works, photochromic materials doped into DNA have shown another potential functionality. Normally, the photochromic dye contents in polymers should be low in order to prevent the phase separation. However, a strong interaction of the photochromic and/or nonlinear dyes with light can be expected by theoretical calculation based on the intercalation of the dyes into stacked layers of nucleic acids within the DNA's double-helix or the trapping within grooves besides the DNA chain, so that dye molecules do not aggregations.

It was presumed that photochromic effect was owing to the interaction between DNA and organic dyes. However, lipids have strong influence on photochromic characteristics.



CL⁻

n-hexadecyltrimethylammonium (CTMA)



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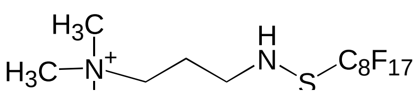
benzylcetyldimethylammonium (CBDA)



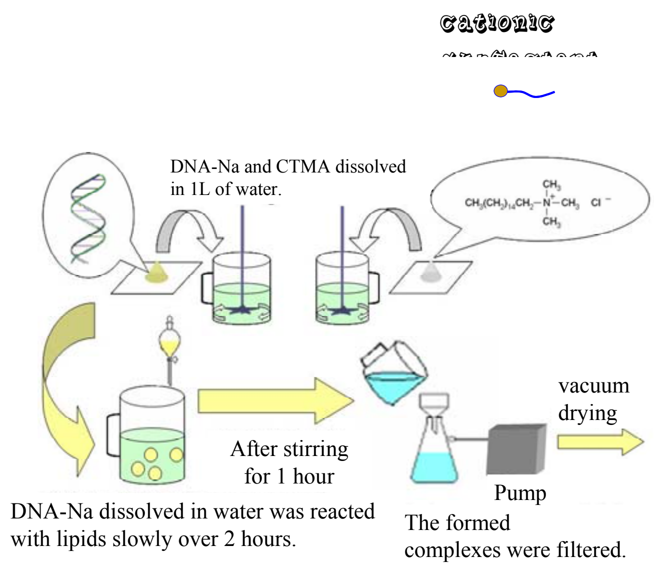


Figure 2. Preparation method of

This paper reports effect of lipids on optical properties of DNA-lipid films. 3 kinds of lipid were used to prepare spiropyran-doped DNA-lipid complexes in order to compare their optical characteristics, such as refractive indices, absorbance and fluorescence intensity.

DNA made from Nippon Chemical Feeding Co. Ltd. was dissolved in distilled water. Lipid in distilled water was mixed with the DNA aqueous solution. 3 different types of lipid were used; single-chain type (CTMA), benzyl type (CBDA), and fluoride type (CF) as shown in Figure 1. Then, the DNA-lipid complex was washed with distilled water, followed by drying process in the vacuum for 24 hours (Figure 2). After drying process, the DNA-lipid complex was dissolved in EtOH:$CHCl_3$=1:4 together with 1,3,3-trimethlindolino-6'- nitrobenzopyrylospiran (SP). Since DNA-CF did not dissolve in EtOH:$CHCl_3$=1:4, only DNA-CF was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol. Finally, the solution was poured into a teflon laboratory dish, followed by drying to evaporate the solvent to obtain films.

At first, CD spectrum was measured to compare with structure of DNA-CTMA and DNA-CBDA. The results are shown in Figure 3. They showed similar CD spectrum as DNA itself. So, it is concluded that the DNA-lipids kept a double helix structure. However, absorption peaks showed red shifts. From these spectra, it is considered that the DNA-lipid structure might be influenced by lipids.

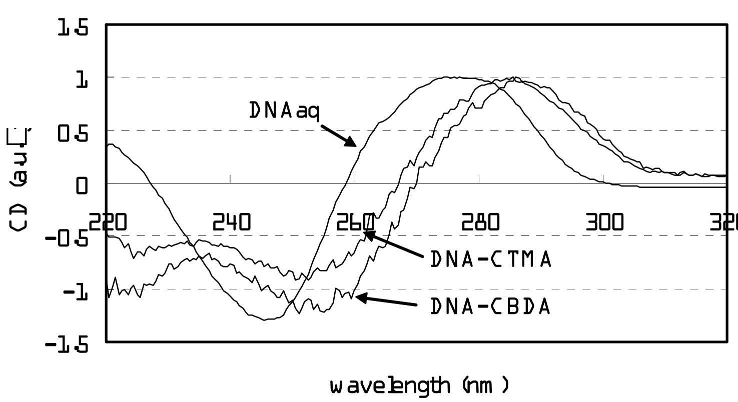


Figure 3. CD spectrum of DNA-CTMA and DNA-CBDA solution in comparison with DNA solution. DNA-CTMA and DNA-CBDA was dissolved in ethanol. DNA-CF could

Basic optical characteristics were measured in terms of refractive indices, absorbance and fluorescence intensity, and photochromic behaviors, of SP-doped DNA-CTMA, DNA-CBDA, or DNA-EF films. DNA-CBDA complex film showed the largest refractive indices as shown in Figure 4. The difference of refractive indexes is ascribed to kinds of lipid, while difference of refractive indices, before and after UV irradiation, was almost similar in both cases.

Absorbance (Figure 5) and fluorescence intensity spectra (Figure 6) of the films were measured to compare with 3 kinds of SP-doped DNA-lipid complexes. Absorbance spectra before UV irradiation showed similar spectrum by themselves, while after UV irradiation, their peaks of absorbance changed depending on kinds of lipid, indicating a blue sift in DNA-EF complex. Fluorescence intensity spectrum showed the same shifts.

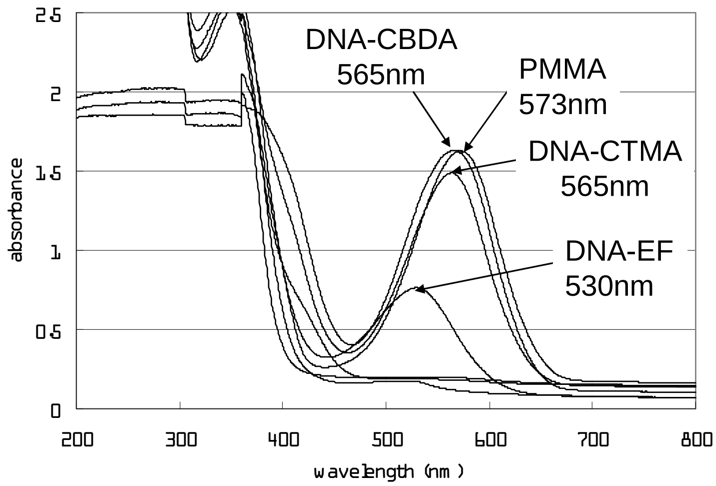


Figure 5. Absorbance spectra of the films were measured to compare with 3 kinds of SP-doped DNA-lipid complexes. Molar ratio of DNA-lipid (or PMMA) : S1=20:1.

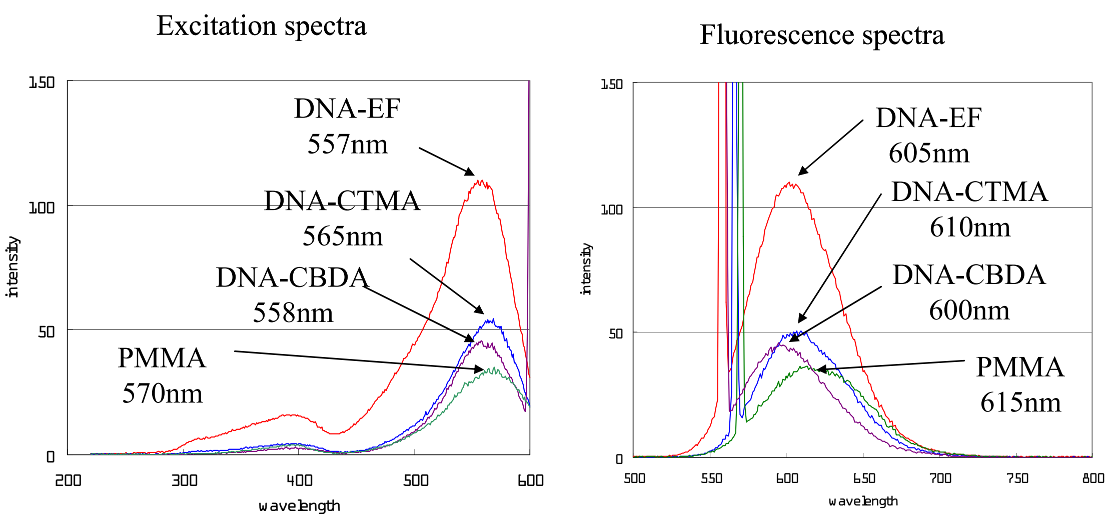


Figure 6. Fluorescence intensity spectra of the films were measured to compare with 3 kinds of SP-doped DNA-lipid complexes. Molar ratio of DNA-lipid (or PMMA) : S1=20:1.

In conclusion, lipids in DNA-lipid complexes caused structural changes of DNA double-helix which resulted in different optical characteristics, possibly owing to the intercalation state changes of dyes within DNA.

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Research 2 Optically-controlled photonic switches based on spiropyran-doped DNA-lipid complex films

1. ABSTRACT

Optical switching properties based on the photochromism of spiropyran-doped DNA-lipid complex films have been studied. On-off switching of the incident light under the alternate excitation of UV- and visible light showed strong dependence of the intensity of the excitation light. We have obtained the switching times of around 200-300ms, but much faster response could be expected since the proportional tendency has not been saturated yet.

2. Introduction

Recent research results on DNA-lipid complexes have shown various attractive features on E/O or O/E devices, optical memories, switches and sensors[1-4]. We have reported[2] possibility of basic optical characteristics, such as refractive indices, absorbance and fluorescence intensity, and photochromic properties, of spiropyran-doped DNA-cetyltrimethilammonium (CTMA) complex films, which have been derived from marine biopolymers, and showed potential application of them to optical switches[5, 6]. Although DNA-lipid complexes showed promising potential for optical functional devices such as switching or signal processing devices, their response speeds were relatively slow to apply them to practical systems. Molecular-chemical bond state of DNA and lipid in DNA-lipid complexes depends on the type of lipid, and consequently optical or photochemical features of DNA-lipid complexes will differ from each other according to the lipid. This may also affect the response speed. Furthermore, it was shown[5, 6] that much faster response speed (switching times) could be attained by increasing the excitation light intensity.

In this paper, we report on switching characteristics of absorption type optical switches based on the photochromic reaction of spiropyran-doped DNA-lipid complex films. We found that the photochromic reaction of those films strongly depended on not only the type of spiropyran but also the excitation intensity. Increasing the excitation intensity both 360-nm UV light for turn-off and 532-nm laser light for turn-on operations resulted in accelerating the response speed in both operations. Response times are almost proportional to the excitation intensity; stronger the intensity, faster the response times. As a result of our experiments, 200-300 ms of response times have been obtained. However, it is limited by the power of our light sources, because the proportional tendency has not been saturated yet, even under maximum radiation power of our equipments. Therefore, much faster response similar to conventional to switches could be expected.

3. Preparation of DNA-lipid complex films

Figure 1 shows our preparation method of DNA-lipid complex films. Single-chain trimethylammonium type lipid (CTMA hereafter) was used to form DNA-lipid complexes. First, refined DNA was dissolved in distilled water. Lipid solution dissolved in distilled water was mixed with the DNA solution[1,2]. Then, the DNA-lipid complex was washed in distilled water, followed by drying process in a vacuum oven for 24 hours at 40□. After drying process, the DNA-lipid

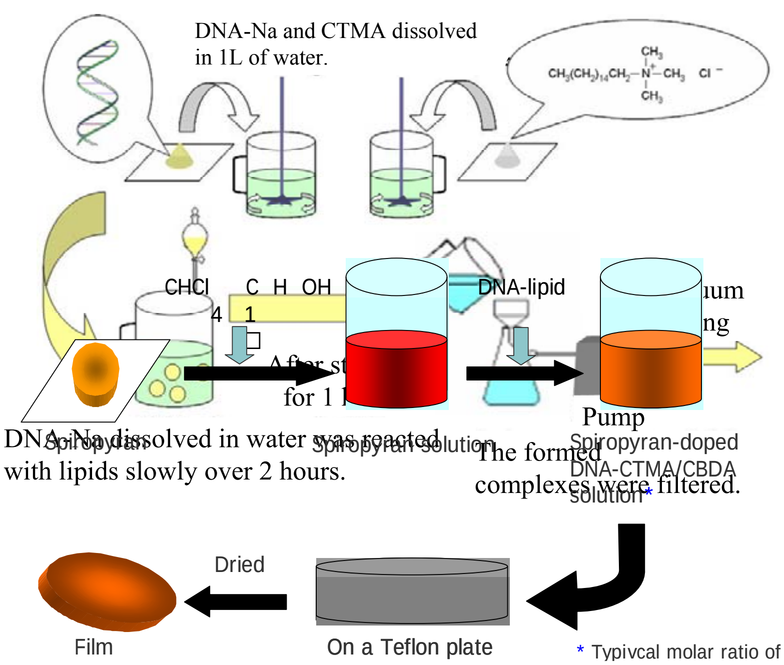


Fig.1. Preparation method of

complex was dissolved in mixed solution (EtOH:$CHCl_3$=1:4) together with spiropyran compounds. Finally, the solution was poured into a teflon laboratory dish, and dried to evaporate the solvent.

Regarding the spiropyran compounds, we used two different types show in Fig. 2; one is the general type of spiropyran containing the nitro group (this spiropyran was labeled "S1" in this report for convenience), and the other is the spiropyran containing the oxazine ring (labeled "S6"). S1-spiropyran shows well-known photochromic reaction with changing its color from light-yellow to purple by UV irradiation. S6-spiropyran changes its color from transparent to blue by UV irradiation, but turns to original state only thermal excitation at room temperature.

As shown in our previous report[5], CD spectrum of DNA-CTMA showed similar spectrum to DNA itself, and consequently DNA-lipids are thought to be keeping the original double helix structure regardless of the types of the lipid. However, small red shift of the CD spectrum peak was observed, and it suggested that the DNA-lipid bond structure might be slightly changed by the type of the lipid.

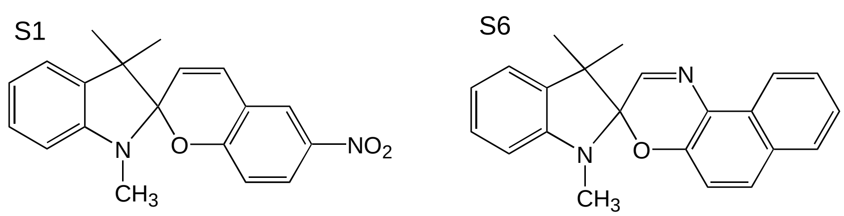
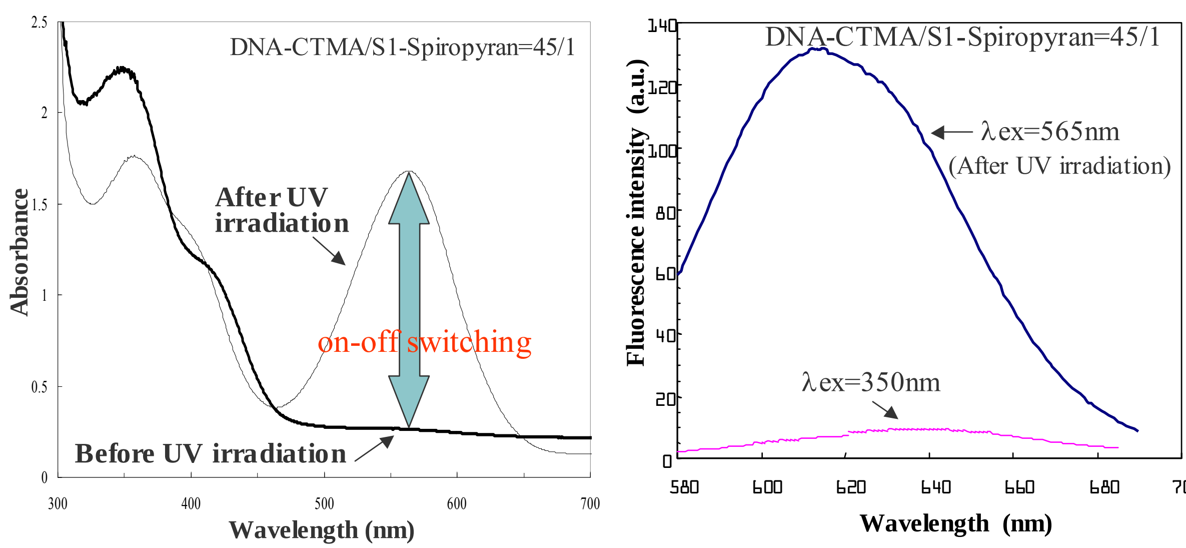


Figure 2. Spiropyran compounds used in this study

4. Switching characteristics of DNA-lipid complex films

4.1 Absorption and fluorescence characteristics of DNA-lipid complex films

The absorption and fluorescence characteristics were measured by using a spectrophotometer and a spectrofluorophotometer made by Shimadzu Corporation. Typical absorption spectra of an S1-spiropyran-doped DNA-CTMA film are shown in Fig.3(a). The absorption spectrum measured in the dark has no distinct absorption peak in the visible region except about 400-nm peak associated with the absorption by the DNA. When the UV light was irradiated on the sample for a sufficient length of time, the absorption spectrum changed and a large absorption peak was appeared at about 560-nm. This change in the absorption spectrum resulted in the change of the color of the film. Figure 3(b) shows the fluorescence spectrum of the same sample. When the sample was excited by UV light, only weak fluorescence at about 630-nm was observed, while the sample showed strong fluorescence at about 610-nm when it was excited by 565-nm light after UV irradiation. This is the typical photochromic reaction. As shown in Fig. 3(a), the spectral change in the absorption peak at 560-nm before and after UV irradiation suggests the possible on-off switching of the incident light around this wavelength. S6-spiropyran doped DNA-CTMA films showed almost similar absorption spectrum change around 620-nm, but it turns rapidly to the original state by thermal excitation at room temperature as reported in our previous report[5].



(a) Absorption (b)

Figure 3. Typical absorption and fluorescence

4.2 Switching operation of DNA-lipid complexes

We examined the switching characteristics of S1- and S6-spiropyran doped DNA-CTMA films. An example of the switching response is shown in Fig. 4. Transmission intensity of incident light at 564-nm was measured under alternate irradiation of UV- and visible light. For the visible light, a 532-nm laser source was utilized. Although the absorbance of was not maximum at this wavelength. The measurement setup of the switching characteristics was shown in Fig. 5.

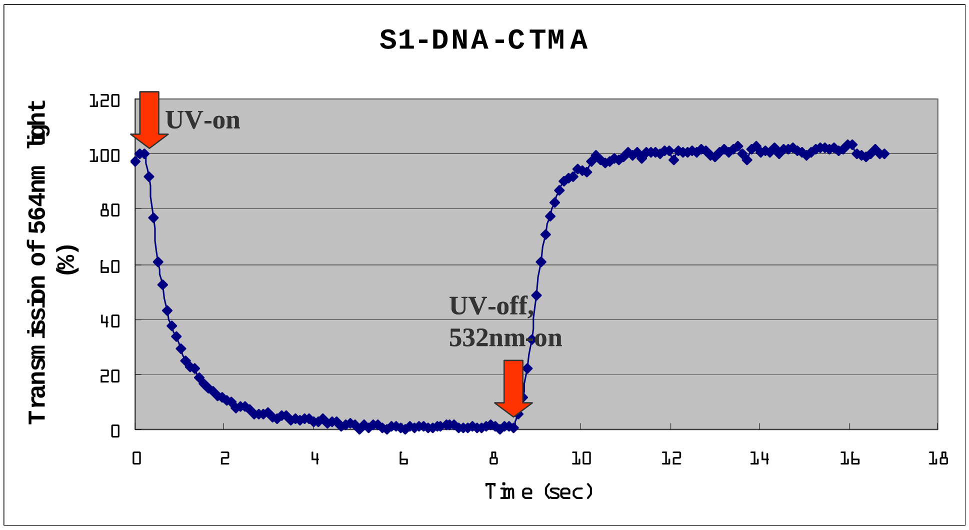


Figure 4. Example of switching operation

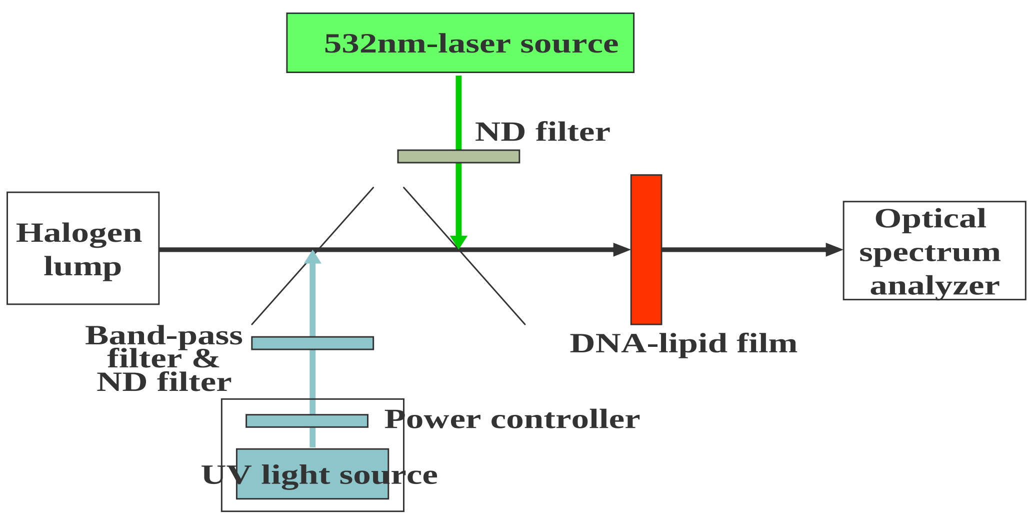


Figure 5. Measurement setup

4.3 Switching Characteristics of DNA-Lipid Complex Films

Switching response of the S1- and S6-spiropyran doped DNA-CTMA films were evaluated by the same setup shown in Fig. 5. The measured excitation intensity dependence of transmission intensity of the incident light at 365-nm are shown in Fig. 6. Figures 6(a) and 6(b) show turn-off and turn-on characteristics of S1-spiropyran-doped DNA-CTMA films, respectively. In both cases, increasing the excitation intensity resulted in faster response. Figure 7 summarizes switching times obtained from the measured response. Regarding S6-spiropyran doped DNA-CTMA films, they showed about 50% faster response than S1-doped ones as indicated in Fig. 7(a). In our experiment, the UV light power was not calibrated, but the maximum green laser power was around 50-mW, and the beam diameter was about 5 mm. However, since the sample holder of the measurement system was tilted away from the incident beam axis, exact value of the excitation light was not calibrated at the surface of the test sample. Therefore, in order to clarify the deference in the intensity dependence, much further considerations should be necessary.

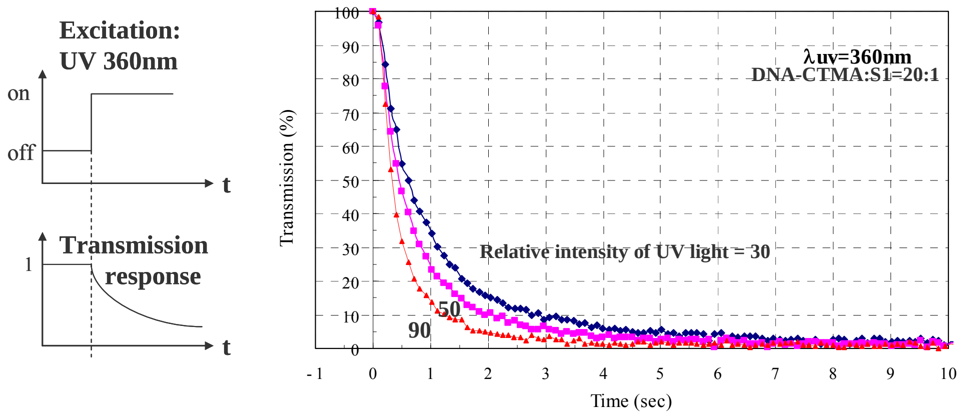


Figure 6 (a) turn-off characteristic

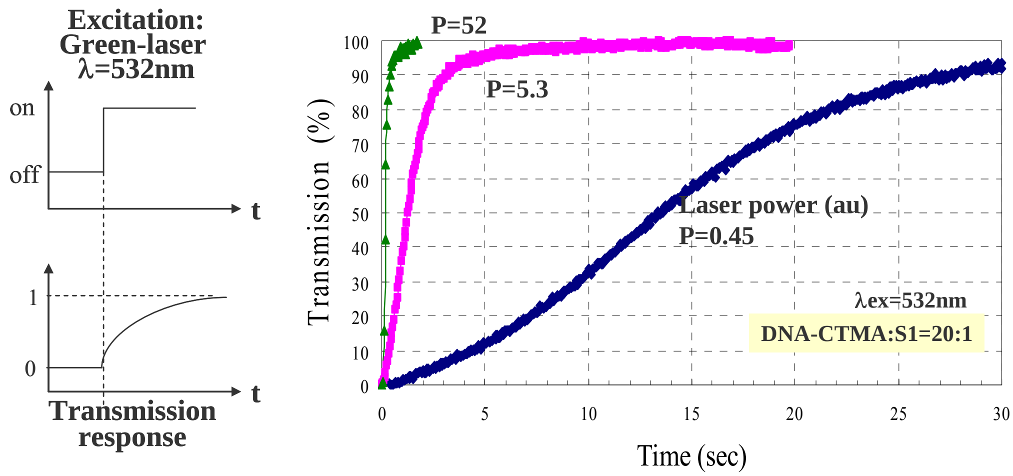
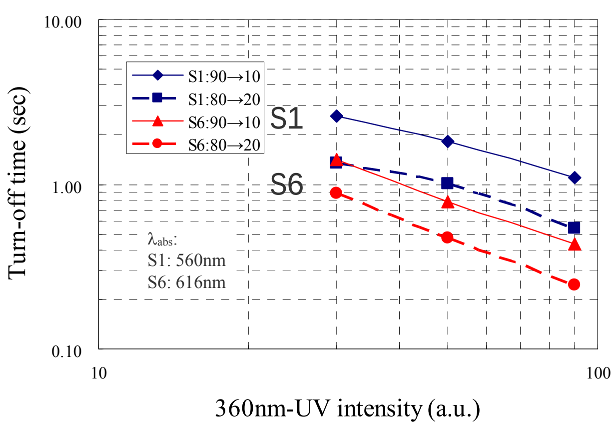


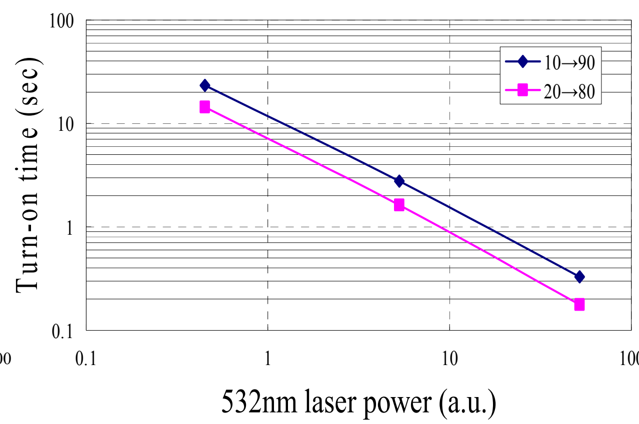
Figure 6 (b) Turn-on characteristic

Figure 6. Switching characteristics of incident light at 565-nm

(Sample: S1-spiropyran doped DNA-CTMA film)



(a) Turn-off times



(b) Turn-on times of

Figure 7. Switching times of spiropyran-doped

The switching time directly depends on the photochromic response speed of the S1-spiropyran doped DNA-lipid films. The photochromic response time from the excited state of the open-ring isomer to the ground state of the closed-ring isomer reflects the decay of the fluorescence intensity. Figure 8 shows the fluorescence decay of the S1-doped DNA-CTMA due to the green laser irradiation. In this case, DNA-lipid solution was used instead of films to simplify the process. The sample was irradiated by the UV-light for a sufficient long period, and then a 532-nm green laser was irradiated at the maximum power in order to turn the spiropyran to the ground state. After rapid rise time for the fluorescence, the fluorescence has decreased within several hundred of milliseconds. This corresponds to the turn-on time shown in Figs. 6 and 7.

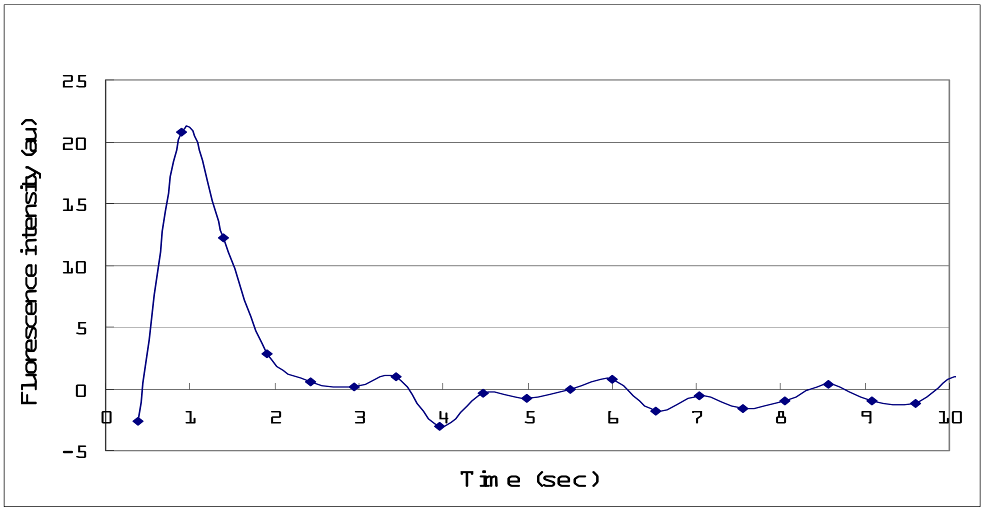


Figure 8. Fluorescence response of S1-spiropyran doped DNA-CTMA films at 640-nm under 532 laser light excitation after sufficient irradiation of UV light.

5. Conclusions

We have reported on switching characteristics of absorption type optical switches based on the photochromic reaction of spiropyran-doped DNA-lipid complex films. We tested S1- and S6-spiropyran doped DNA-CTMA complex films and found that the switching action of those films strongly depended on not only the type of spiropyran but also the excitation intensity. Increasing the excitation intensity of both 360-nm UV light for turn-off and 532-nm laser light for turn-on operations resulted in accelerating the switching speed in both operations. Switching times are almost proportional to the excitation intensity, stronger the intensity, faster the switching times. S6-spiropyrans showed faster response than S1-spiropyrans. Although S6-spiropyran could not realize perfect optically controlled switches because of their partial thermo-chromic properties.

At present, 200-300 ms of response times have been obtained, but they seemed to be limited by the power of our light sources. Since the proportional tendency has not been saturated yet, even under maximum radiation power of our equipments, much faster response similar to conventional to switches could be expected. However, a strong irradiation of the excitation light generally induces some degradation of the photochromic operation of the dyes. Therefore, there may be some tradeoff between excitation power and response times. In conclusion, all our results indicated the potential of DNA-based optical switches by proper selection of the type of spiropyran with proper combination of the control light intensity.

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Research 3 Structure-property relations of intercalated DNA-lipid complexes

1. ABSTRACT

Various DNA-cationic lipid complexes and their bulk films were prepared and their physical properties were measured. Consequently, it was found that physical properties were greatly dependent on each lipids. The DNA-lipid complexes film formed by C-12 lipid of single-chain trimethylammonium type showed the largest value on mechanical strength. Water absorption behaviors of the films were also dependent on kinds of lipids. It was found that fluorescence quantum yields of cyanine-intercalated DNA-lipid films decreased nonlinearly with increasing relative humidity, while the fluorescence quantum yields were high compared with that of PMMA in whole range of relative humidity. Orientation of dye-intercalated DNA molecules was investigated under magnetic field to enhance orientations of dye molecules in DNA.

2. Experimental

2.1 Synthesis of DNA-lipid complexes

At first, fibrous DNA-Na was dissolved in distilled water (6.5g / L) with stirring by a mechanical stirrer. One liter of the aqueous solution of DNA-Na was added to one liter of aqueous solution of various lipids (twice molar against sodium cation of DNA-Na), and a DNA-lipid complex was precipitated. The precipitate was collected by filtration, washed with distilled water, and then dried in a vacuum oven at 40 C. Following lipids which are shown in Fig. 1, were used to form DNA-lipid complexes by the same method as mentioned above.

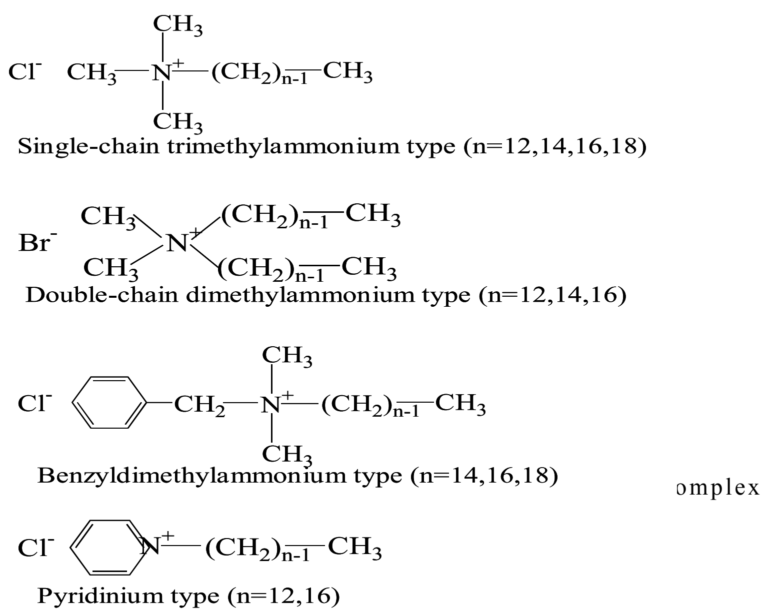


Fig. 1 Kinds of lipids used for

2.2 Preparation of DNA-lipid complexes cast film

At first DNA-lipid complexes were dissolved in ethanol/chloroform=1/3(volume ratio) with concentration of 0.06g/ml. And dodecyl trimethylammonium, stearyl trimethylammonium and dodecyl pyridinium were dissolved with concentration of 0.03g/ml. After dissolution of the DNA-lipid complexes, these solutions were cast into teflon plates, and the films were obtained by evaporating the solvent in a drying oven at 40 C.

2.3 Measurement of mechanical properties of the films

The cast films of DNA-lipid complexes were cut off in size of 4x0.5cm, and then the films was adjusted to absorb humidity by leaving them in desiccators of 63% and 100% R.H. for more than two days at ambient temperature. Mechanical strength of the films was measured by stretching the films until it fractured by stretching test machine of AGS-5LNH Shimazu. Co. Ltd.

2.4 Quantum yield of fluorescence light

Quantum yield of the dye-intercalated DNA-lipid films was measured. Schematic diagram for the experimental setup was shown in Fig. 2. For the measurement, we employed the integrating sphere, and located the sample film within the integrating sphere. As a light

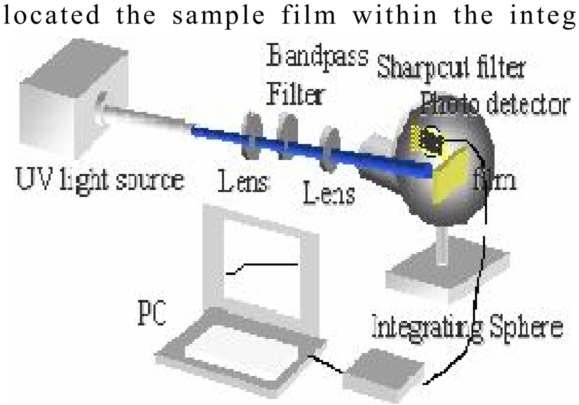


Fig. 2 Experimental setup for the measurement of fluorescent quantum yield

source, a xenon lamp was used. The light beam was focused by lens system, and monochromatic light was obtained by band path filter. The emission from sample film was detected by photodiode and was then depicted by a PC.

2.5 Orientation of DNA-CTMA complex under magnetic field

Orientation of DNA-CTMA complex which was intercalated by various dyes was carried out under magnetic fields of various strength which were applied to DNA-CTMA-dye methanol solutions while evaporating to form films. The experiments were carried out at the National High Magnet Center at Tsukuba in March.

3. RESULTS AND DISCUSION

3.1 Mechanical properties of DNA-lipid complexes films

Various papers [1-11] were reported on DNA-lipid complexes, while non of papers described effects of lipid kinds on mechanical properties of the DNA-lipid complex films, so mechanical properties of the DNA-lipid complex films were measured in terms of tensile strengthes.

Results of stretching tests in 63% and 100% R.H. of DNA-lipid complexes films prepared from various kinds of lipids indicated that the film of n=12 indicated about twice strength compared with the film of n=16 at 63%R.H., while the strength decreased 1/3 under 100% R.H. when compared with it under 63% R.H. On the other hand, strain increased under 100% R.H.. From this phenomenon, effect of plasticity of adsorbed water in the films was found to be rather large.

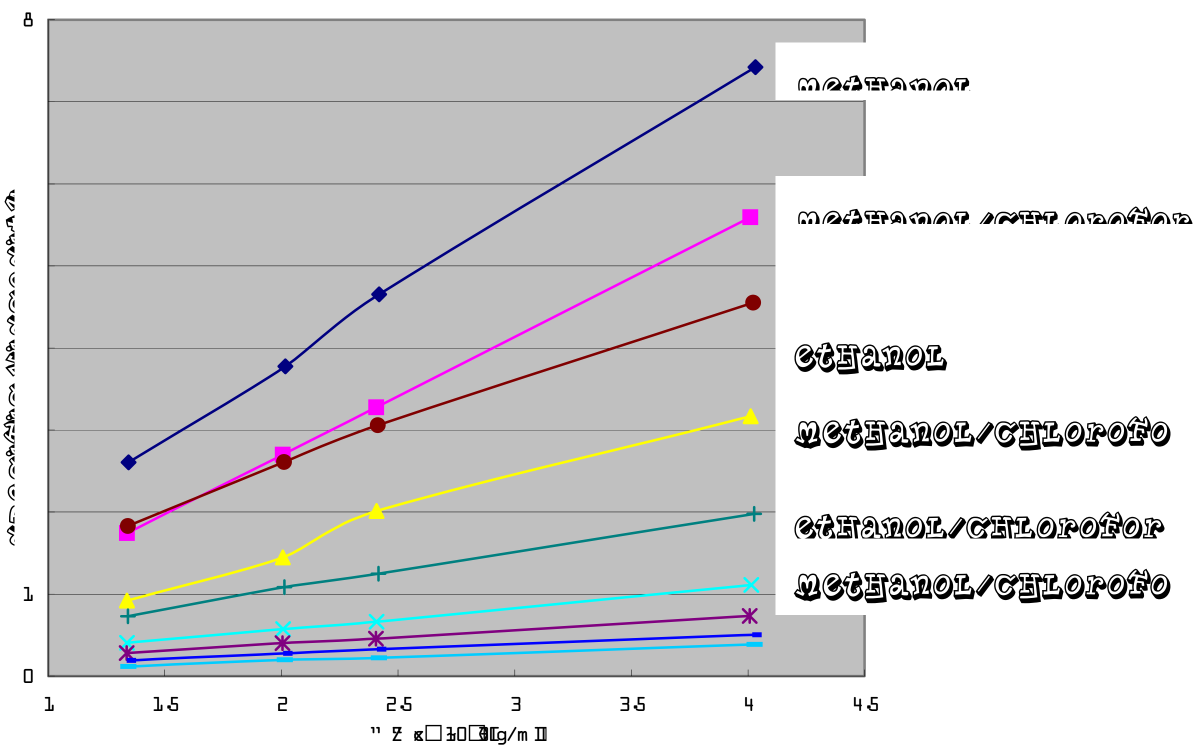
From these results it was revealed that the kinds of lipid had a very large influence on mechanical properties of DNA-lipid complexes films. When only strength and strain of the films were taken into consideration, lipid of single-chain trimethyl ammonium type was the best in terms of mechanical properties.

Relationship of relative humidity and initial Young's modulus derived from the S-S curves of the films is collectively shown in Table 1. In any case initial Young's modulus decreased and became soft by increasing relative humidity. Single-chain trimethyl ammonium n=12 had the highest value of initial Young's modulus among lipids. Subsequently, the values are arranged in order of pyridinium n=12 > single-chain trimethyl ammonium n=16 > double-chain dimethyl ammonium n=16 > pyridinium n=16 > benzyl dimethyl ammonium n=14 > benzyl dimethyl ammonium n=16 > double-chain dimethyl ammonium n=12. These results indicated that the kinds of lipids had large influences in terms of hardness of the films.

Table 1 Initial Young's modulus of DNA-lipid films under

Lipid	R.H.(%)	Young's Modulus(MPa)
single-chain type n=12	63	940
	100	179
single-chain type n=16	63	405
	100	53
pyridinium type n=12	63	573
	100	64
pyridinium type [illegible]	63	209
	[illegible]	[illegible]

In order to investigate effects of solvents for the conformation of DNA-CTMA molecules in solutions, specific viscosities of the DNA-CMA solutions in various mixed solvents were measured and results are shown in Fig. 3 which indicated that methanol as a solvent gave a high specific viscosity, while increasing amount of chloroform to methanol decreased the specific viscosity of the solutions and ethanol solution had less specific viscosity than methanol solution. These results indicated that the conformation of DNA-CTMA molecules was dependent on kinds of solvents and DNA-CTMA molecules in methanol had much stretched structures than in ethanol. It becomes clear that conformations of the DNA-CTMA molecules in solutions influenced tensile strength of the DNA-CTMA films as entanglement of DNA molecules would be changed during the film processing. Further research on the solvent effects is now being carried out.



methanol/chlorofo

concn. x10-3 (g/ml)

Fig 3 Effects of solvents on specific viscosity of DNA-CTMA solutions

3.2 Fluorescence quantum yields of DNA-double chain dimethyl ammonium complexes films and orientation of DNA molecules under magnetic field

Fluorescence quantum yields of the cyanine doped DNA-double chain dimethyl ammonium (n=12, 14 and 16) complexes films which had the lowest values of moisture absorption and the cyanine-doped PMMA film were measured under relative humidity of 0, 36, 63, 80 and 100%. Fluorescence quantum yields of these films are shown in Fig.4. It was found that fluorescence quantum yields of DNA-lipid films decreased nonlinearly with increasing relative humidity, while the fluorescence quantum yields were high in comparison with that of PMMA in whole range of relative humidity. From these results it was found that absorbed water gave inferior influence on optical property, while DNA-lipids complexes gave a favorable influence compared with general materials such as PMMA. these results are important for the design of optical device performances

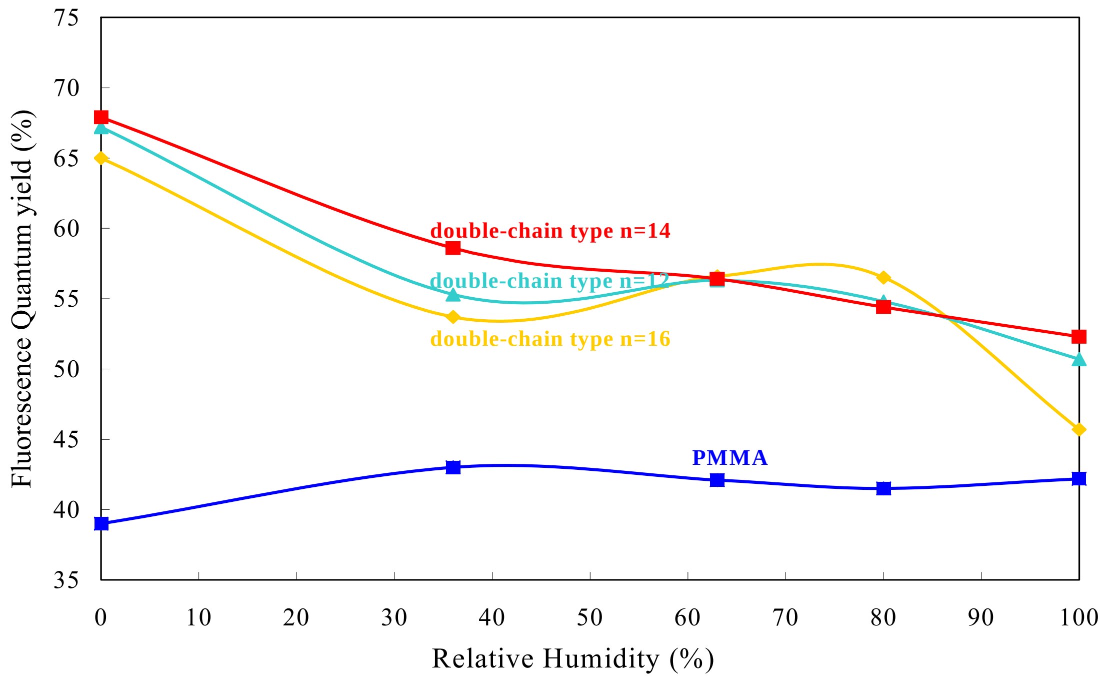


Fig.4 Fluorescence quantum yield of DNA-double chain

Orientations of DNA molecules under various strength of magnetic fields mere measured by polarized microscopic analyses as shown in Fig.5 which indicated that magnetic filed caused orientation of DNA molecules.

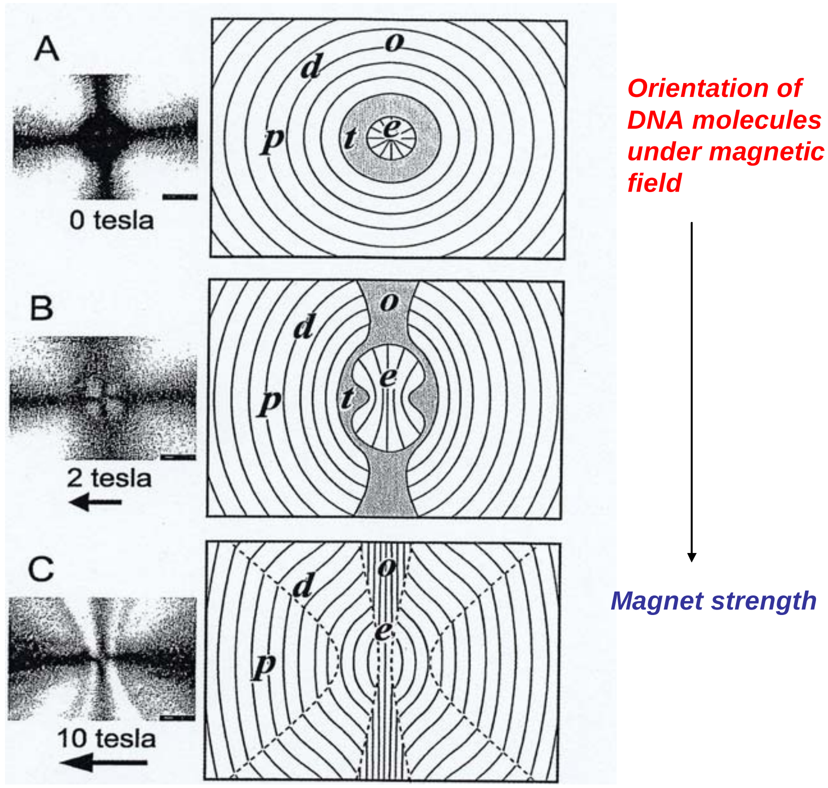
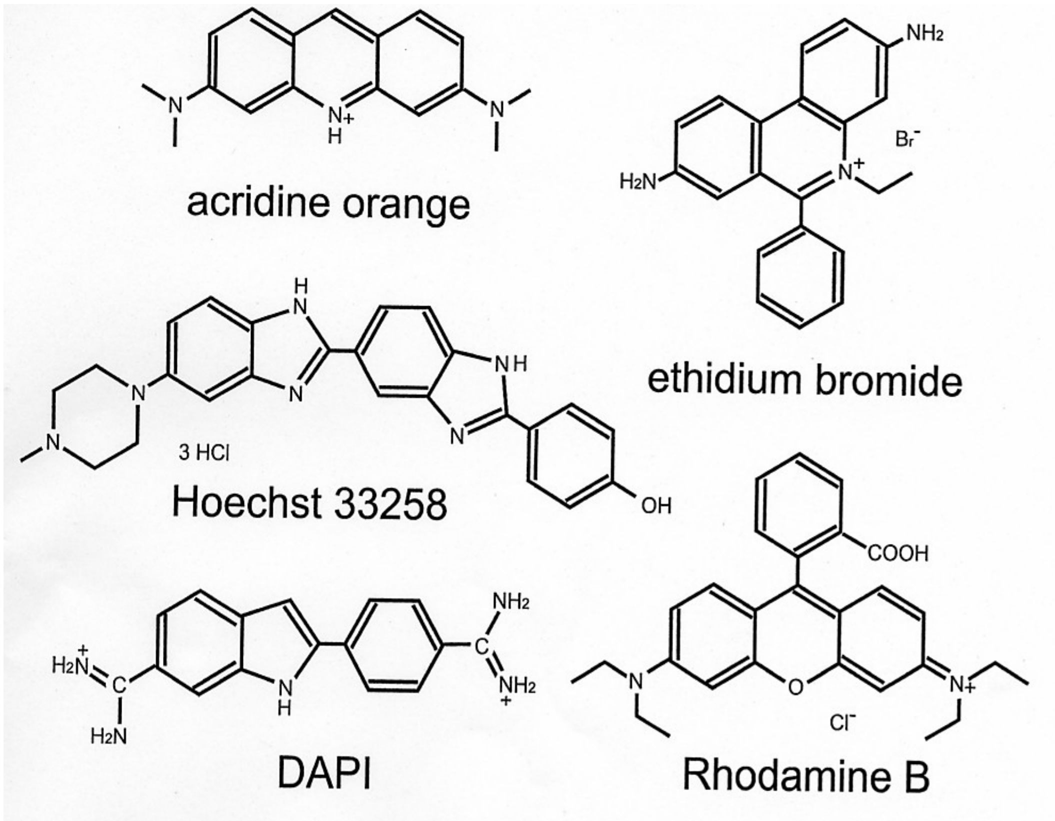
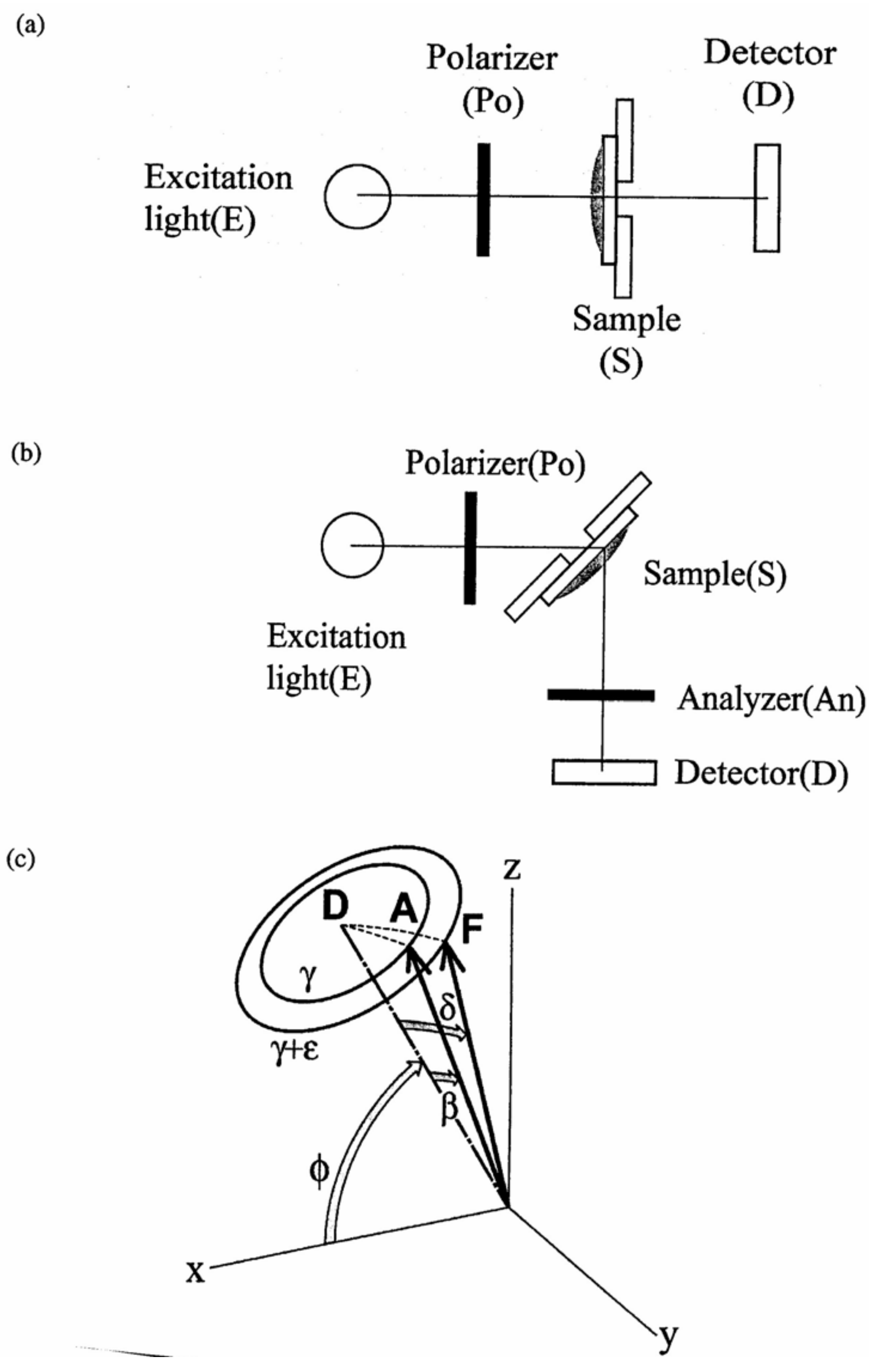


Fig. 5 Polarized microscopic pictures of DNA-CTMA films prepared under various magnetic fields.

In order to investigate the orientation of dye molecules which were intercalated into the double helix of DNA, following dues were intercalated into DNA molecules in aqueous solutions to obtain thin films:

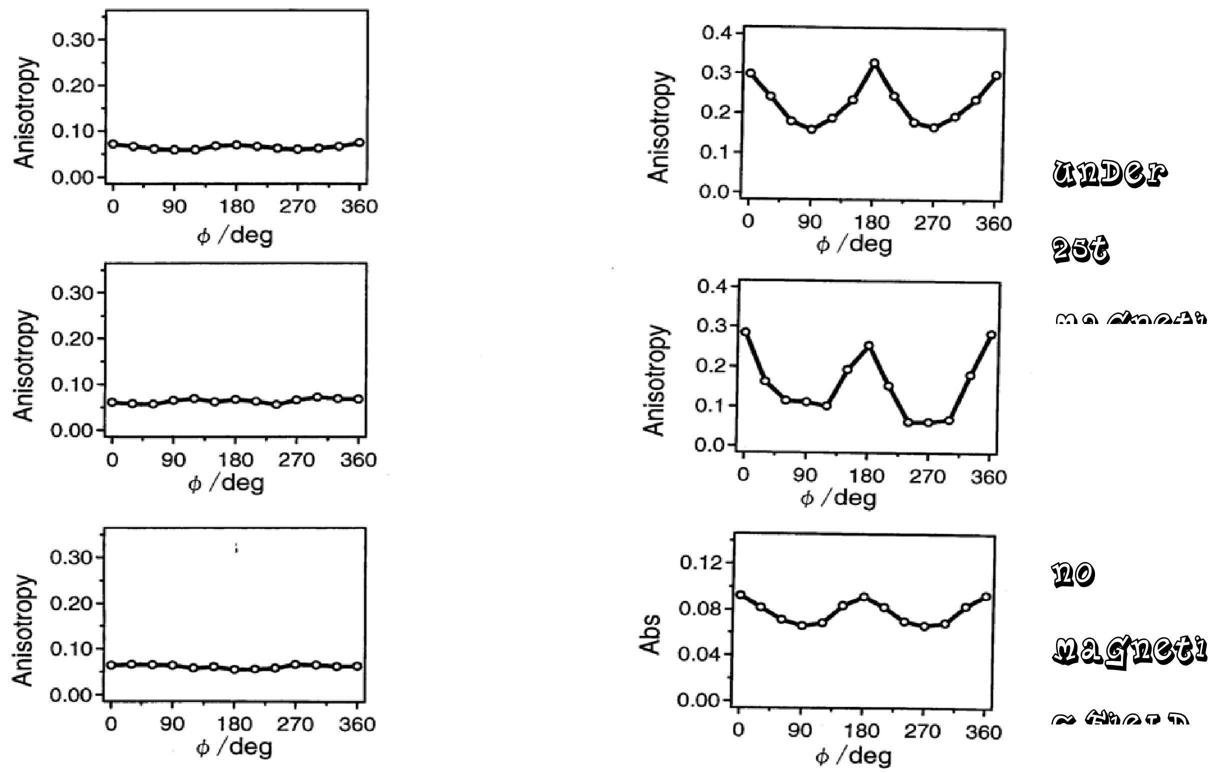


The dye-intercalated DNA films were irradiated under 12T magnetic power to orient dye molecules.
The orientations of dye molecules were measured by using a rotating polarized fluorescence spectroscopic method as shown in Fig. 6. Fluorescence intensities as functions of rotating angles of various dye-intercalated DNA films were measured as shown in Figs. 7 and 8. Results of fluorescence intensities as functions of rotating angles indicate peaks at about 90 ^{o} angle, clearly suggesting the orientations of dye molecules in DNA double helix under magnetic field.



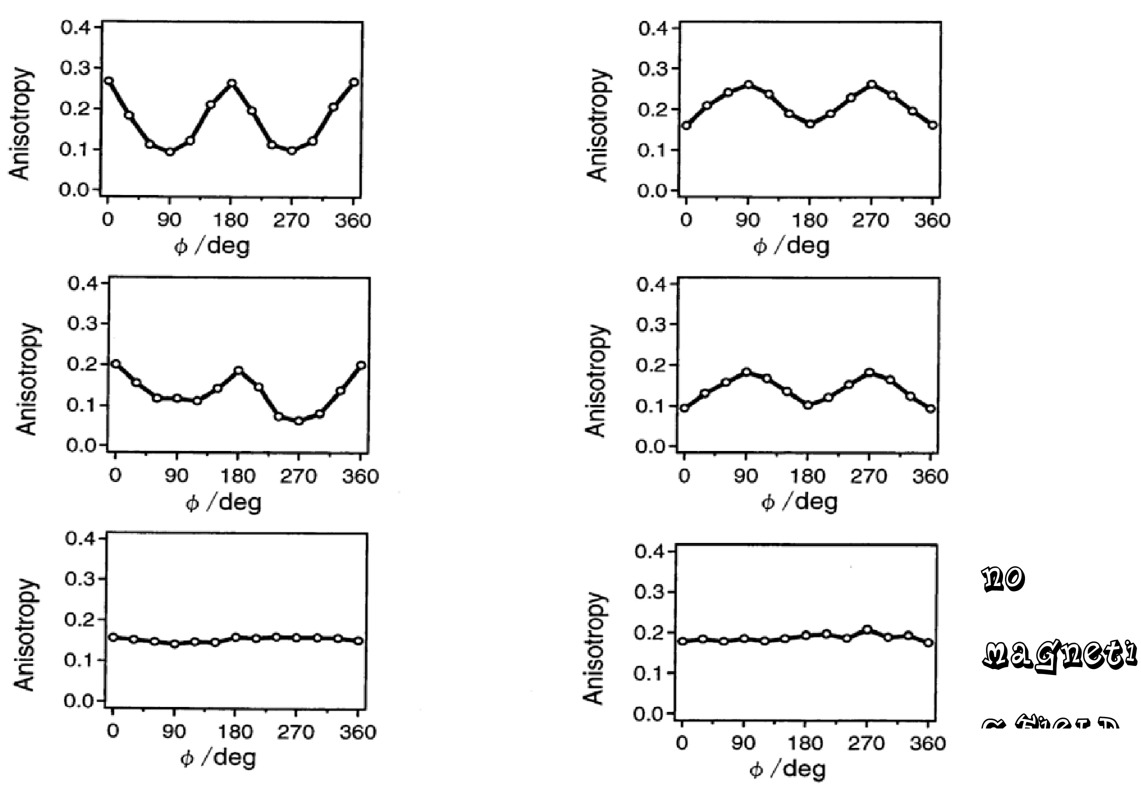
(a)
Polarizer
(Po)
Detector
(D)
Excitation
light(E)
Sample
(S)
(b)
Polarizer(Po)
Sample(S)
Excitation
light(E)
Analyzer(An)
Detector(D)
(c)
z
D
A
F
γ
γ+ε
δ
β
φ
x
y

Fig. 6 Rotating fluorescence spectroscopic measurement



RohdB-DNA film   KN5A-DNA film

Fig. 7 Fluorescence intensity dependence of dye-DNA films as functions of rotating angles



EtdB-DNA DAPI-DNA film

Fig. 8 Fluorescence intensity dependence of Dye-DNA films as function of rotating angles

Effect of magnetic strength on the enhancement of quantum yields of optical dyes for fluorescence emission will be investigated in near future and results will be summarized soon..

5. References

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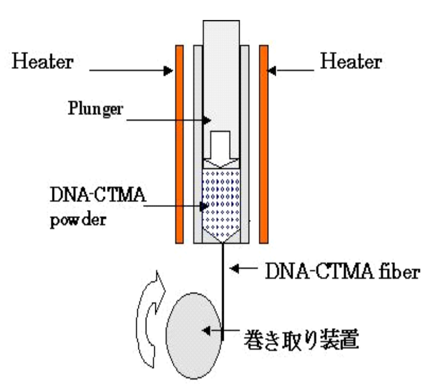
Research 4 Fabrication of intercalated DNA-lipid complexes to fibers and films

Processing of novel photonic materials derived from Marine DNA was investigated in terms of optical fibers which was reported that optical characteristics of DNA films was greatly improved by intercalating organic dyes into base pair layers of DNA molecules. This year aimed at optical fiber processing by melt processing of DNA-lipid complexes which were intercalated by organic optical dyes into the DNA fibers.

Melt-spinning of DNA-CTMA complex was performed by following spinning machine:

Melt-spinning machine



SEM picture of DNA-CTMA Fiber

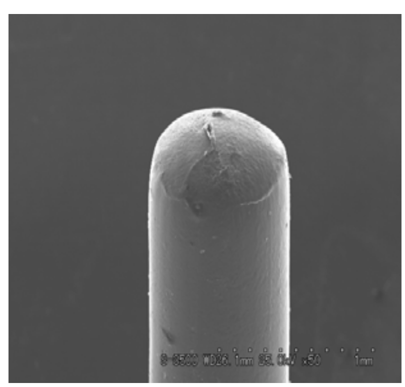


Fig. 1 Melt-spinning machine for DNA-□□□□ complex

Fluorescence light emission of the dye-doped DNA fibers was measured by an experimental set-up shown in Fig. 2.

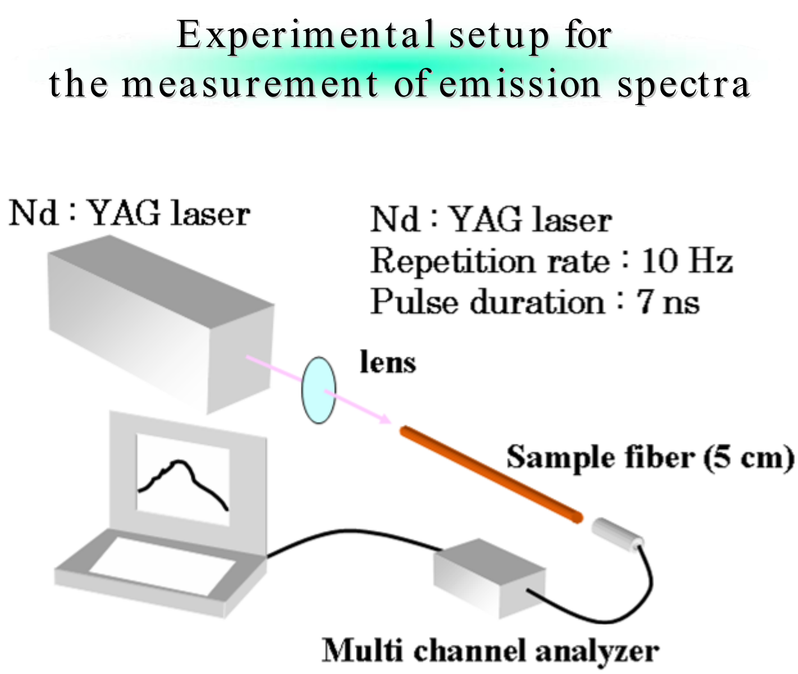
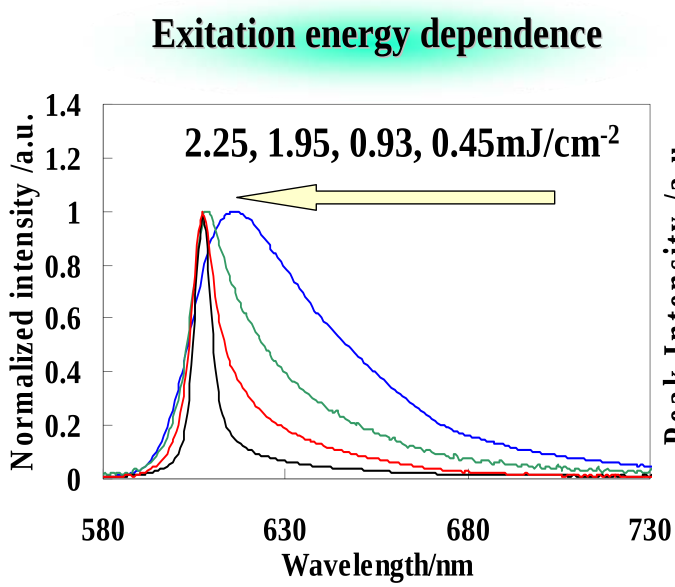
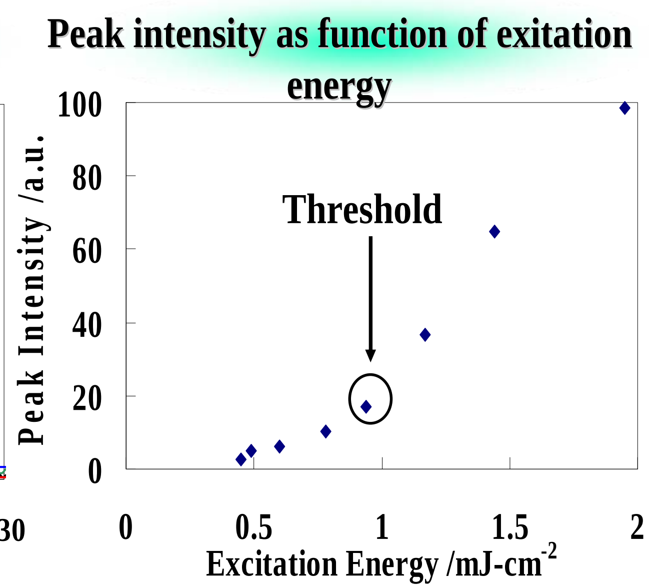


Fig. 2 Experimental set-up to measure emission spectra

Results are shown in Fig. 3 which indicates that lasing occurred with increasing power of exitation light and an amplified spontaneous emission (ASE) was observed with narrowing width of spectra. The threthold value was less than 1 mJ.cm-2 which was very low for lasing. These results suggest that the dye-doped DNA fibers are very much promising for light amplification for telcommunications.

Lasing of dye-doped DNA fiber





Dye-DNA fiber

Dye: 3.6wt%

Diameter: 1mm

Fiber length: 5cm

Narrrowing of spectrum width

⇩

ASE emission

(Amplified Spontaneous emission)

Fig 3　Lasing phenomena of dye-doped DNA fiber

Over

Report of Budget in 2005

Labor Cost	
Senior Personnel(PI)	$2,000
Other (Postdoc, Dr. Yamaoka)	$11,000
Total Labor cost	**$13,000**
Direct Cost	
Equipment	0
Travel	$550
Materials and Supplies	$5,950
Publications and Reports	$500
Total direct cost	**$5,000**
Total Overhead Cost	**$5,000**
Total Project Value	**$25,000**

Date of This Report: January 31, 2006

Reported by Naoya Ogata
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Signed by Naoya Ogata

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January 31st, 2006

Dr. Misoon Y. Mah

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7-23-17 Roppongi, Minato-ku
Tokyo 106-0032

Dear Misoon:.

Enclosed here I am sending the Final Report in 2005 for the research project "*Self Assembled Nano-Photonic Devices Derived from Marine DNA for Opto-Electronic Applications*".

Best regards,

Naoya Ogata
Professor Emeritus,
Ogata Research Laboratory
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